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Short Communications

The Dissociation Constant of Silver Fluoride

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The emf of the following cell was measured at 25° C

$$\text{Ag, AgCl} \;\Big|\; \begin{matrix} c_{Ag}\ \text{C}\ AgClO_4 \\ c_F\ \text{C NaF} \\ (1-c_{Ag}-c_F)\ \text{C}\ NaClO_4 \end{matrix} \;\Big|\; 1\ \text{C}\ NaClO_4 \;\Big|\; 1\ \text{C}\ NaClO_4 \;\Big|\; \text{Hg, } Hg_2SO_4$$

The solutions to the left were made by adding aqueous sodium fluoride from a burette to a solution of silver and sodium perchlorate in the electrode vessel. Experimental details were the same as described in some previous papers on complex formation *Cf. e. g.* [1,2].

Some of the results are tabulated in Table 1, where E is the difference between the emf of the initial cell, where $c_F = 0$, and the emf of the same cell after the addition of fluoride. The concentration of free silver ions, $[Ag^+]$, has been calculated from Nernst's formula *Cf,* [2], and then β_1 was computed from equation 1.

Table 1. Titration of silver ions with fluoride.

$c_{Ag} \cdot 10^3$	$c_F \cdot 10^3$	E mV	β_1 C^{-1}	$c_{Ag} \cdot 10^3$	$c_F \cdot 10^3$	E mV	β_1 C^{-1}
10.51	0	0		105.1	0	0	
8.47	118	6.8	0.47	95.0	243	2.6	0.46
7.51	174	10.6	0.46	93.5	274	3.0	0.47
6.74	218	13.9	0.47	92.4	299	3.3	0.48
6.11	255	16.9	0.49	90.6	337	3.8	0.50
5.15	310	21.9	0.48	89.6	365	4.1	0.50
4.38	355	26.6	0.49				
3.50	405	33.1	0.51				
		Mean:	0.48			Mean:	0.48

This paper is a part of a study of the complex formation between silver and halogen

$$\beta_1 = \frac{[AgF]}{[Ag^+]\ [F^-]} = \frac{c_{Ag} - [Ag^+]}{[Ag^+] \cdot [c_F - (c_{Ag} - [Ag^+])]} \qquad (1)$$

The computation shows that AgF is the only complex formed in noteworthy concentrations. The slight increase of β_1, for increasing c_F could be interpreted as a formation of AgF_2^-, but liquid junction potentials and changes of activity coefficients make it impossible to draw any certain conclusion. Neither are polynuclear complexes formed, as the calculated β_1, remains constant, when c_{Ag} increases from 0.01 to 0.1 C.

Hence the dissociation constant of AgF, $1/\beta_1$, = 2.1 C at the ionic strength 1 C ($NaClO_4$).

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1. Leden, I. Diss. (1943) Lund.
2. Leden, I. *Acta Chem. Scand.* 3 (1949) 1318.

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